Concentration Profile of Glass Fiber Bundles in Epoxy-Based Gradient Composites During Centrifugation

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ABSTRACT: The short fiber bundles separated from the machining waste of a printed circuit board (PCB) manufacturing plant were used in preparing functionally graded composites using polysulfide-modified epoxy resin. The graded material was developed using centrifugation technique. The centrifugation time was varied to obtain different gradient profiles. The concentration profile was then compared with the theoretical HD model (Hashmi-Dwivedi model), which was modified to accommodate the changes in the shape of suspending particles. A shape factor was introduced in terminal velocity estimation. The simulated results are in agreement with the experimental trends. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3840–3846, 2009

Key words: centrifugal casting; FGM; epoxy resin; concentration profile; glass fiber; fiber motion

INTRODUCTION

Functionally gradient material (FGM) is a new class of material that is obtained by different processing technologies. The use of gradient composite in place of conventional composite may provide some special properties like smooth stress transition, unique characteristics at different positions, use of low amount of costly filler, desired properties with distance, etc.[1–6]

The various fabrication methods used are solidification process, chemical vapor deposition, spray atomization, co-deposition, powder metallurgy techniques, and centrifugal casting in the metal matrix-based FGMs. The centrifugal casting is considered the most economical and attractive process.[7–9] The centrifugation technique has been used recently in making graded distribution of carbon fiber and graphite in epoxy resin matrix in polymer matrix-based FGMs.[10,11] Lee et al.[12] prepared gradient composites using carbon fiber and epoxy resin and characterized it for mechanical strength. Funabashi[13] reported the electrical conductivity of nickel-coated carbon fiber-filled epoxy gradient composite. The performance of FGMs depends on the concentration profile and the uniform dispersion in the matrix. A few studies have reported on the measuring gradients using X-ray attenuation, laser confocal microscopy, microstructure, measurement of dielectric strength, or abrasive wear of material.[11,14] The character of motion of particles moving in viscous fluid is still hotly debated, particularly in concentrated dispersions.[15,16] Gao and Wang[7] reported a model by incorporating solidification process during centrifugal casting of FGMs. The model equation was solved numerically using a fixed grid finite volume method. Hashmi-Dwivedi (HD) model has been used to estimate the concentration of spherical particles in polymerizing fluid under gravitational and centrifugal force, and experimental results were validated for calcium carbonate particles.[17,18] In the present study, this HD model was further modified for fiber bundles instead of particles by taking shape factor into account.

The objectives of the present work are to develop graded composites using short glass fiber (GF) bundles separated from cutting waste of printed circuit board, and a modified approach could be used to estimate the concentration profile of fiber bundles moving in a matrix, which is getting polymerized with time during centrifugal casting of FGM at different cross sections of sample.

MATERIALS AND METHODS

Room temperature cured polysulfide-modified epoxy resin used in this study was obtained from Choksey Chemicals, India. The density of epoxy resin cured at room temperature with hardener in the ratio of 2 : 1 was 1.115 g/cc. GF bundles separated from machining waste of a printed circuit

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board manufacturing plant in waste form were obtained from GNVFC, Barodara (India). These fibers were separated in our laboratory using a separation column.[19] The spherical equivalent diameter of fiber (fiber assumed as spherical particles having equivalent volume) varies from 30 to 110 μm. The density of GF bundles was 1.53 g/cc, as estimated by a relative density bottle.

Sample preparation

The simple centrifugal arrangement was developed in the laboratory, as reported in previous studies.[17,18] A electrical current-controlled motor was used to rotate shaft at a fixed speed. Sample molds were fixed at both ends of a bar, which was fixed on shaft of the motor by appropriate clamping arrangement. A tachometer was attached to observe revolution per minute (rpm) of the assembly. GF bundles were added to a mix of epoxy resin and hardener and were thoroughly mixed. The mix contains 3 vol % of GF bundles in the resin system, which was transferred to two identical molds. The molds were closed and fitted on the centrifugal arrangement. The molds are designed to make cylindrical pins of diameter 10 mm. Parameters were adjusted such that GF bundle experienced a centrifugal force equivalent to 100 times the gravitational force. The acceleration due to gravity is assumed 9.8 m/s^2. The centrifugal system that produces acceleration equal to 980 m/s^2 was used in this experiment. Mainly two parameters, radial distance (r) and angular velocity (ω), can produce desired acceleration (a) as per following relation

$$a = r\omega^2.$$

In this relation, angular velocity influences "acceleration" significantly as compared to radial distance, and therefore small changes in position of suspending particles was considered negligible. Furthermore, the acceleration diminishes quickly under the influence of resistance offered by viscous medium, and a constant terminal velocity is attained by the moving particles in a very short time. The time of centrifugation was varied as 1, 2, 3, and 30 min. Thereafter, molds were removed from the rotating system and kept at room temperature for 24 h. The cured samples were subjected to density tests.

Morphological study

Scanning electron microscope (SEM) JEOL-35 CF was used to observe the morphology of fiber. Fibers were gold coated before observing the surfaces.

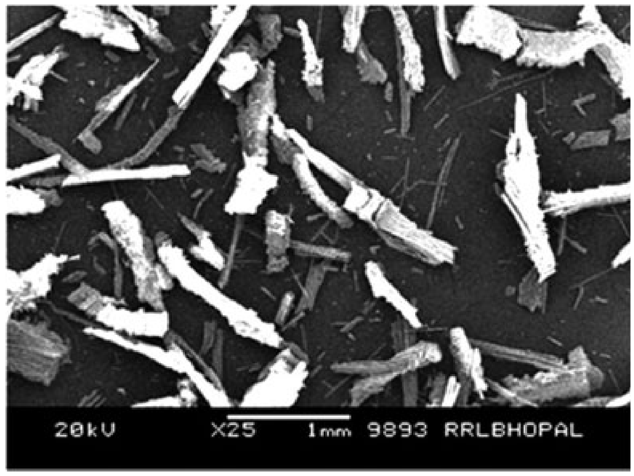

Figure 1 SEM of glass fibers used in this study.

Optical microscopy

Distribution pattern of GF in the epoxy matrix was observed by using a Lietz optical microscope at 50 times magnification. Before observing the surface, the sample was polished using a polishing cloth. Distribution of GFs in the different zones was observed under the transmission mode of optical microscope.

Density test

Densities of the functionally gradient polymeric composites were determined by cutting the discs into 1.5-mm thickness from the cylindrical pins. The density of the specimen was measured by a Mettler Toledo machine using Archimedes principle.

RESULTS AND DISCUSSION

Figure 1 shows the SEM of GF bundles used in this study, which were separated by gravity separation method. It is seen that short GFs are in bundle form. GF bundles exhibit irregular shapes of different sizes. The length of these irregular shape bundles is sufficiently higher than their lateral dimension and resembles to nonuniform cylindrical objects.

Figure 2 depicts the schematic diagrams of fiber dispersion in (a) noncentrifuged and (b) centrifuged samples. The fiber distribution was assumed uniform in a noncentrifuged sample, as shown in Figure 2(a). The centrifuged sample shows a gradient as the outcome of movement of fibers in polymerizing liquid, as shown in Figure 2(b). The movement of suspension in the polymerizing fluid depends on density difference between fibers and fluid, rate of curing of polymerizing fluid, shape and size of fibers, bulk viscosity of medium, centrifugal force, centrifugal time, etc. The longer fiber experienced higher force corresponding to higher mass and

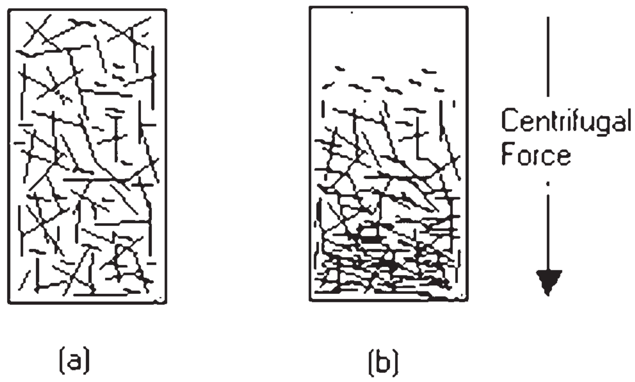

Figure 2 Schematic diagram of (a) noncentrifuged and (b) centrifuged samples.

hence moved faster to accumulate near the end of the sample. The shorter fibers experienced lower force and moved slow in the polymerizing fluid. More fibers are visible in the bottom portion, whereas the top portion wherein negligible GFs were observed shows a fiber-free zone.

Figure 3 shows the microstructures of different regions of a graded composite made by using GF bundles distributed in polysulfide-modified epoxy resin. The sample was prepared centrifuging the uniformly distributed GF bundles in epoxy resin for 2 min. The specimen pin was cut in such a way to observe the distribution of particles in the sample, including top clear zone, middle zone, and bottom zone. For this purpose, a thin sheet of 1.0 mm thickness was cut parallel to centrifugal force. Micrographs were obtained under transmission mode of optical microscope. The dark portions represent GF bundles, whereas epoxy resin is in light shade. It is difficult to focus on individual fibers under transmission mode of optical microscopy. The large numbers of GF bundles positioned at different planes were observed in the form of dark areas. Three regions of this sample are shown in Figure 3(a–c).

Figure 3(a) shows a micrograph of clear zone in which epoxy-rich portion at top with negligible GFs was observed. Figure 3(b) shows the micrograph at 15 mm from top. In this micrograph, concentration of GF is slightly increased. Short fibers are visible in this region. Figure 3(c) shows the micrograph near the packed bottom zone at 25 mm distance from top. At high GF concentration, light could not be transmitted as observed in Figure 3(c). This micrograph exhibits accumulation of GF bundles near the packed region due to boundary restriction.

Figure 4 shows the experimental results on variation in concentration of GF bundles (in terms of density) in the graded composite with distance. The experimental conditions have been given in the section "Materials and Methods" under the subheading "Sample Preparation". These curves reveal that specimens have graded structure, which was controlled by centrifugation time. The specimen that centrifuged for highest time period (i.e., 30 min) exhibited the maximum density at the bottom of the pin and minimum density at the top. For the short time of centrifugation, less accumulation of GF at the bottom region was observed. Noncentrifuged sample exhibited almost uniform distribution at different positions.

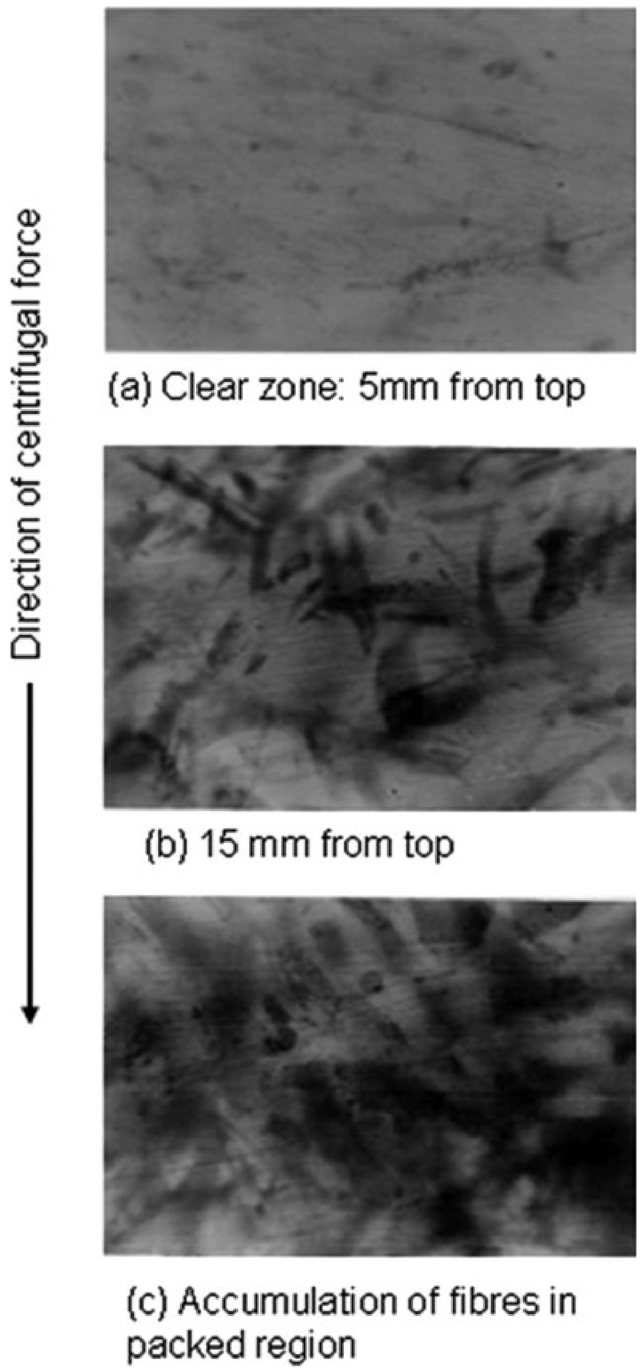

Figure 3 Optical micrographs of 2-min centrifuged sample at different positions.

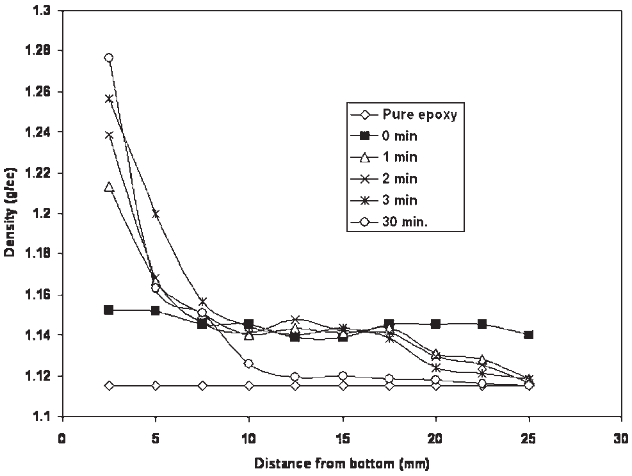

Figure 4 Graph showing gradual changes in density with position for different samples.

A careful observation also reveals that a sample centrifuged for 30 min has mainly two regions: one a graded concentration profile that spans up to 12.5 mm from the bottom, and the second region that is almost a clear zone spreading from 12.5 to 25 mm from the bottom. On the other hand, specimens prepared in 1, 2, or 3 min show two different concentration profiles in each sample; one profile that spans up to 10 mm from the bottom and second that spans from 17 to 25 mm from the bottom. Between these two profiles, a region of almost constant concentration was observed.

In ideal conditions of sedimentation, mainly three zones are observed, like top clear zone, bottom sediment zone, and a middle zone. In this ideal condition with elapse of time, clear zone and sediment zone would increase but middle zone shall shrink and after some time shall extinct. The variation in fiber size and hindrance effect would bring about changes, and the middle zone could be converted to a graded material with uniform transition from fully packed to fiber-free zone.

The motion of particles in a concentrated suspension under gravity or centrifugal forces is a complex process.[17] The complexity increases further when the fluid itself changes its characteristics with time, for example a polymerizing fluid. Theoretical understanding of this phenomenon was considered, as described in previous studies.[17,18] HD model has been used recently to determine terminal velocity of spherical particles under gravity and centrifugal forces in a polymerizing fluid and is shown below,[17]

$$v_m = D^2(\rho_s - \rho_1)r\omega^2(1-\phi_s)^{4.65}/(18\,\mu_0 e^{bt_c}) \qquad (1)$$

where D is diameter of spherical particle, ρ_s density of solid, ρ_l density of liquid, r is the radial distance from the axis of rotation, ω is angular velocity, μ_o is initial viscosity of polymerizing fluid, t_c is time elapsed in polymerizing, b is a constant that is derived from cure kinetics of polymerizing fluid, ϕ_s is volume fraction of suspending particles present in the fluid.

This approach[17,18] was further modified for predicting the concentration of irregular shaped particles, such as GF bundles, in epoxy resin. For this purpose, an assumption that "The irregular shaped GF bundles were considered as spherical particles having equivalent volume" was made.

Accordingly, the above equation took the following form,

$$v_m = D_f^2(\rho_s - \rho_1)r\omega^2(1-\phi_s)^{4.65}/(18\,\mu_0 e^{bt_c}) \qquad (2)$$

where D_f is diameter of sphere having equivalent volume of corresponding GF bundle. The velocity of particles in a fluid depends on the resistance offered by the fluid in contact of particles. The increased surface area of a particle shall increase the resistance and therefore there is a need to introduce a shape factor in the model. To take care of the shape of GF bundle, shape factor was included, which is defined as follows

$$\text{Shape factor}, (S_f) = \text{Surface area of sphere} \,/\, \text{Surface area of GF bundles}$$

For spherical particle, value of shape factor is 1.0. The value of shape factor decreases with increasing L/D ratio of fiber bundle and with increasing representation surface area of fiber bundle. After introducing shape factor, the terminal velocity can be determined using the following equation,

$$v_m = D_f^2\, S_f(\rho_s - \rho_1)r\omega^2(1-\phi_s)^{4.65}/(18\,\mu_0 e^{bt_c}) \qquad (3)$$

where S_f stands for shape factor. Equation (3) was used to determine velocity of GF bundles corresponding to r and an initial homogeneous volume fraction of fibers in polymerizing fluid.

To observe the concentration profile of GF bundles at a particular time and place under centrifugal force using eq. (3), simulation was performed and results are discussed subsequently. The distance covered by the GF bundle in each second was estimated from velocity of GF bundle, assuming that the clear zone traveled with the GF bundle speed. The volume fraction of GF bundles for the next set of data on new position was computed assuming uniform distribution of GF bundle. During each step, GF bundle velocity was computed, and volume fraction of GF bundles was estimated with changes in viscosity of resin with elapsed time. For computing sediment zone, maximum 0.36 volume fraction was taken that was experimentally evaluated, and the GF bundle

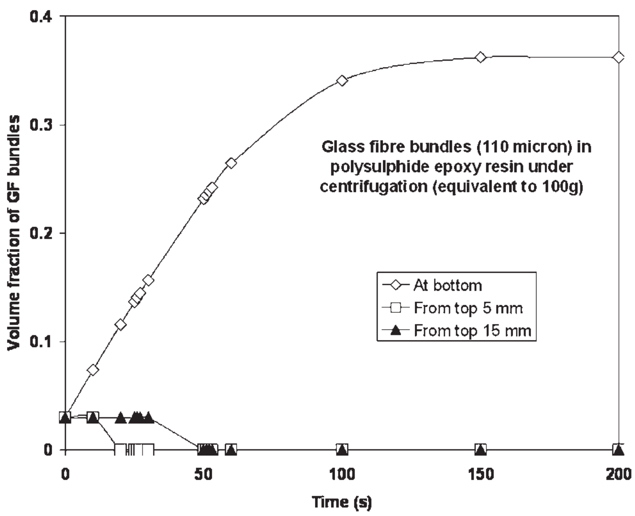

Figure 5 Predicted volume fraction of GF bundles versus time for 110 μm size at different places.

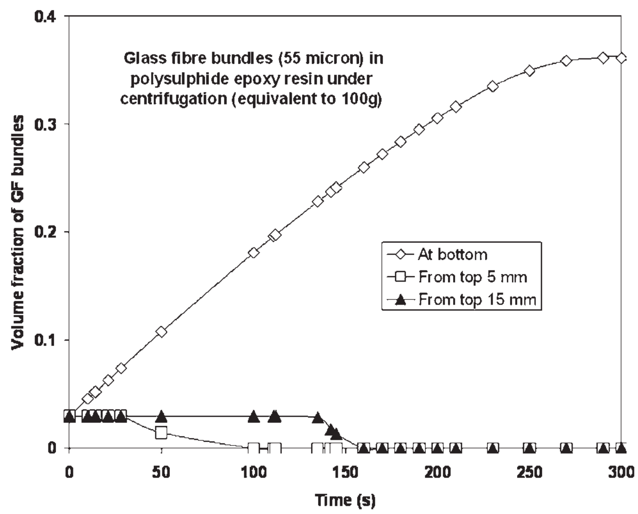

Figure 6 Predicted volume fraction of GF bundles versus time for 55 μm size at different places.

velocity was assumed to be zero at this volume fraction. The details of simulation have been reported elsewhere.[17,18]

Figure 5 shows variation in volume fraction of GF bundles against time in seconds for 110 μm GF bundle. A line parallel to x-axis shows constant volume fraction of GF bundles. The volume fraction of GF bundles either increases or decreases depending on the position in the sample. Near the bottom or the dead end of sample at a distance of 1 mm, the volume fraction increases quickly and reaches the maximum level of 0.36 volume fraction. Thereafter, further increase was stopped and no more movements of GF bundles were predicted. At 5 mm from the top portion of sample, the concentration remained constant for almost 12 s and thereafter it reduced to become zero, corresponding to fiber-free zone. Similarly at 15 mm distance from the top, the volume fraction of GF remained constant at 0.03 for more than 34 s and thereafter reduced to zero in almost 22 s. It is obvious that the rate of increase in volume fraction near the bottom or the rate of decrease in volume fraction at the initial part of sample is higher, which reduced with the time elapsed due to the viscosity and hindrance effects in these systems.

Figures 6 and 7 are shown to compare the changes in concentration profiles for different sizes of GF bundles. As depicted from Figure 6, the smaller the GF size slower would be the speed as compared to their larger counterparts. In both the simulation, three different positions were observed; the bottom position, top position, and a middle position. The bottom position is filled faster by larger-sized GF bundles as compared to short-sized GF bundles. Similarly, clear zone propagation is faster in Figure 6 as compared to Figure 7. The middle zone (15 mm from top) becomes clear in 150 s, by 55 μm size GF bundles; however, there was no change in the concentration of GF bundles having 30 μm size in the middle zone, as shown in Figure 7.

In the present case, the size of GF bundle is nonuniform and a mixture of different particle sizes is present in the sample. The different sizes of GF bundles would move with different velocities. When constant centrifugal force was applied, the fibers settled at different speeds because of the different masses of fibers. The larger fiber bundles would settle faster than the shorter ones. As a consequence, the bottom region would be rich in larger GF bundles, and the upper region would be rich in the shorter GF bundles. The concentration profile could be predicted by combining the volume fraction of each type of GF bundles at particular distance and

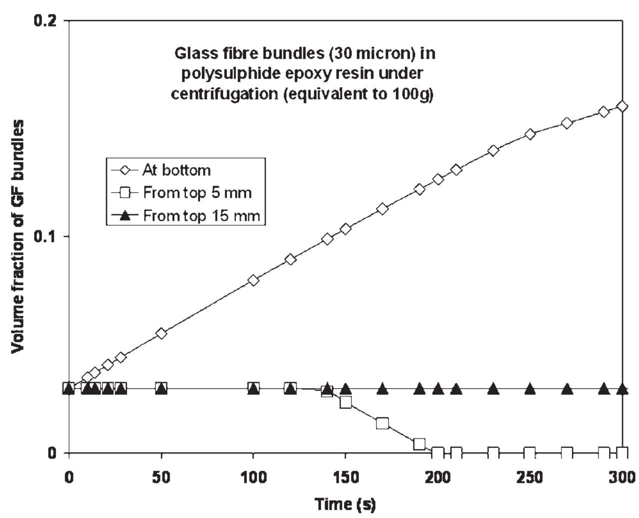

Figure 7 Predicted volume fraction of GF bundles versus time for 30 μm size at different places.

at particular time. Similarly, it can be extended to correlate with the distribution of particles and a nearly real concentration profile is expected. For a mixture of GF bundles of three different sizes, the concentration profile is expected to have a beginning from finer particles profile and ending with larger particle profile due to the velocity differences. A simulation is given in Figure 8 that shows variation in GF volume fraction against time for multisized GF bundles. In this sample, GF bundles of 30, 55, 110 μm sizes were in proportion of 20, 30 and 50, respectively. The overall 3 vol % of fiber bundles in the resin was kept fixed also in this simulation. Therefore, GF bundles of 30, 55, 110 μm sizes present in the system were in 0.6, 0.9 and 1.5 vol %, respectively The change in volume fractions was affected by multisized system and was not smooth but appeared in steps, which were reflecting particular size of the GF bundles. In the present simulation, only three sizes were considered; therefore, a three-step reduction in volume fraction was observed.

The results of model prediction were experimentally validated. For this purpose, the composition of 3 vol % GF bundles was fixed. Time of centrifugation was varied at 0, 1, 2, 3, 30 min. The experimental results are given in Figure 4, and conditions are given in "Sample Preparation." The predicted volume percent of GF bundles in graded material with measured volume percent of GF bundles are plotted in Figure 9. The experimental values are little different than the predicted values of volume fractions of GF bundles. Two lines drawn parallel to predicted values show that all experimental values lie within the predicted values ±0.06. The departure from the ideal conditions may be attributed to a few important factors; (a) nonuniform particle size of GF bundles that varies from 30 to 110 μm instead of a fixed

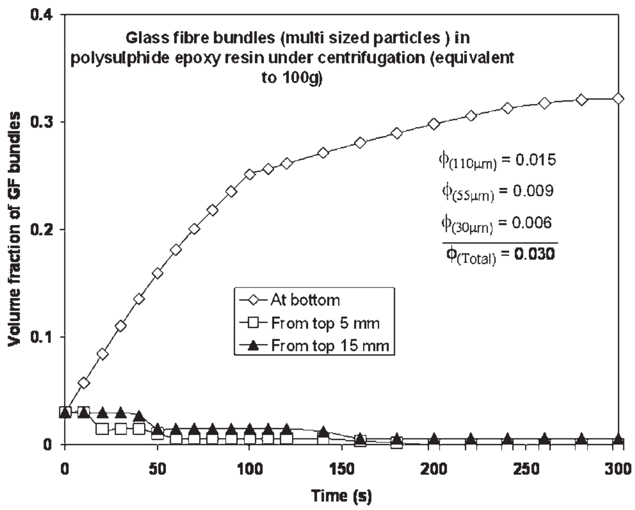

Figure 8 Predicted volume fraction of multisized GF bundles (30, 55, 110 μm) versus time at different positions.

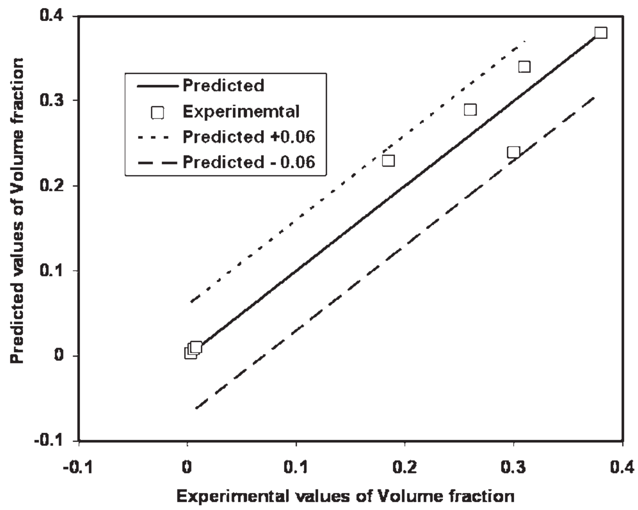

Figure 9 Plot showing differences in experimental versus predicted values of volume fractions of glass fiber bundles.

size, (b) the possible agglomeration of GF bundles, (c) fiber alignment causing resistance in fiber movement during application of centrifugal force as shown schematically in Figure 2. Most of the bundles aligned perpendicular to the centrifugal force direction because a cylindrical body experiences torque and rotates to the horizontal direction in viscous liquid, as the center of gravity and mass of gravity do not coincide. When force is applied, the fibers tend to make both gravities coincide to take static state.[12] The other reason for aligning fiber is the crowd of fibers that depress the fiber network in the centrifugal direction to make shifting of the fiber orientation distribution toward perpendicular to the force direction. Another reason for departing the experimental results with theoretical results is the problems associated with reporting the actual density of graded samples at a specified position. For example, in the present case, the centrifuged samples in the form of pins having 10 mm diameter and 30 mm length were obtained. The pins were sliced into disc form having 1.5 mm thickness. The reported density in this case is the average density instead of the actual density corresponding to the particular positions.

CONCLUSIONS

Glass fiber epoxy-graded composites were successfully developed by centrifugation method. Gradual profile in concentration of GF bundles could be controlled by varying time periods. A modified approach for evaluating velocity and concentration changes of GF bundles dispersed in composite under centrifugal force has been applied that takes into account the change of viscosity of dispersion medium with time and irregular shape of fiber bundles. The approach has been validated with experiments. The results are in agreement with the trends obtained by simulation.

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